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Influences of mechanical pre-treatment on the non-biological treatment of municipal wastewater by forward osmosis

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Abstract

Municipal wastewater treatment commonly involves mechanical, biological and chemical treatment steps as state-of-the-art technologies for protecting the environment from adverse effects. The biological treatment step consumes the most energy and can create greenhouse gases. This study investigates municipal wastewater treatment without the biological treatment step, including the effects of different pre-treatment configurations, e.g., direct membrane filtration before forward osmosis. Forward osmosis was tested using raw wastewater and wastewater subjected to different types of mechanical pre-treatment, e.g., microsieving and microfiltration permeation, as a potential technology for municipal wastewater treatment. Forward osmosis was performed using thin-film-composite, Aquaporin Inside^{TM} and HTI membranes with NaCl as the draw solution. Both types of forward osmosis membranes were tested in parallel for the different types of pre-treated feed and evaluated in terms of water flux and solute rejection, i.e., biochemical oxygen demand and total and soluble phosphorus contents. The Aquaporin and HTI membranes achieved a stable water flux with rejection rates of more than 96% for biochemical oxygen demand and total and soluble phosphorus, regardless of the type of mechanical pre-treated wastewater considered. This result indicates that forward osmosis membranes can tolerate exposure to municipal waste water and that the permeate can fulfil the Swedish discharge limits for small- and medium-sized wastewater treatment plants.

Key words: biomimetic membrane, forward osmosis, membrane fouling, microfiltration, microsieving, wastewater treatment

Introduction

Given the increasing environmental concern of nutrient depletion and water scarcity, municipal wastewater is starting to be considered as a valuable nutrient and water resource.[1] Wastewater can be treated mechanically, biologically and/or chemically to prevent oxygen depletion and eutrophication in receiving water bodies. During biological treatment, most carbon and nitrogen is converted to carbon dioxide (CO_2) and nitrogen gas (N_2), respectively. The formation of CO_2 and N_2 can result in the formation and release of nitrous oxide gas (N_2O), which significantly contributes to the greenhouse effect.[2]

Ravazzini et al. [3] introduced direct membrane filtration (DMF) for municipal wastewater treatment without biological treatment. In this process, raw municipal wastewater is directly applied to a membrane without any biological pre-treatment. The direct membrane filtration concept has been tested using microfiltration (MF) [4] ultrafiltration (UF) [3] and direct capillary nanofiltration [5] with different types of wastewater, e.g., raw municipal wastewater,[3,4,6,7] domestic wastewater,[8] greywater,[9,10] and effluents from the primary.[3,11] These studies demonstrated that the produced permeate was particle free and of good quality for its intended purposes, such as irrigation. However, direct MF and UF discharge do not fulfil the present Swedish standards for wastewater treatment plants.[12,13] Because these standards are expected to become even more stringent in the future,[14] alternative/additional treatment steps should be considered.

One method for achieving higher water quality is to use reverse osmosis (RO), which produces higher purity permeates. However, because RO requires high trans membrane pressure (TMP), this increased purity comes at the cost of a high energy

demand and an increased propensity for membrane fouling. An alternative could be forward osmosis (FO) because FO has recently been shown to achieve solute rejections as high as RO.[15,16] FO is driven by an osmotic pressure gradient across a selectively permeable membrane, which allows water molecules to migrate from a feed solution (FS) with a low osmotic pressure, such as wastewater, to a draw solution with a high osmotic pressure, such as seawater. Because the FO process is operated in the absence of applied hydraulic pressure, this process has an intrinsically lower fouling propensity and requires less energy than RO.[17]

These advantages of the FO process have led to more than 1000 studies during the last decade for different applications. However, only 7% of these studies are related to wastewater treatment.[18] Most of these studies focused on using synthetic wastewater as feed for FO processes [19-22], and only a few studies have been performed using real diluted raw municipal wastewater.[15,23] Furthermore, Xie et al. [16] reviewed different membrane-based processes for nutrient recovery and used FO as the sole technology for treating urine, synthetic wastewater and activated sludge. Wang et al. [15] recently published a study using real diluted municipal wastewater with solute rejections of ammonium and total nitrogen (TNt) of 68% and 48%, respectively, and rejections of chemical oxygen demand (COD) and total phosphorus (TPt) of more than 99%.

However, the integration of existing wastewater mechanical pre-treatment methods such as microsieving (MS) and microfiltration (MF) with FO in terms of water flux, solute rejection and fouling characterisation has not been widely reported in the literature and is therefore a novel approach.

The purpose of this study is to assess FO as a sole technology for wastewater treatment of the main stream without a biological treatment step at small- and medium-

sized WWTPs in Sweden. The study investigates the use of mechanical pre-treatment steps such as microsieving and microfiltration prior to FO, with sodium chloride as a model draw solution. The impacts of mechanical pre-treatment on water flux and solute rejection are evaluated.

Material and methods

Raw municipal wastewater of medium strength was collected after screening (6 mm perforated plate screens, EscaMax, Huber AG, Germany) and sand and grit removal at the Källby WWTP (120 000 population equivalent) in Lund, Sweden (Figure 1). This wastewater was then used as FS in FO during Experiment 1 (Exp. 1), which is denoted as Raw. A portion of the wastewater from the grit-chamber was introduced to a pilot plant and was equipped with a rotating drum filter with a filter-cloth with an aperture size of 100 µm (HDF801-1H, Hydrotech AB, Sweden) and a MF unit with a nominal pore size 0.2 µm (MFP2, Alfa Laval A/S, Denmark). MF experiments were conducted at 0.03 bar TMP.[24] The microsieve filtrate (MSF) and microsieve (MS) plus MF permeate (MFP), respectively, were used as FS for FO experiments 2 (Exp. 2) and 3 (Exp. 3), see Figure 1.

FO membranes

Two types of flat-sheet thin-film-composite (TFC) membranes were used in this study: one from Aquaporin A/S (Copenhagen, Denmark) and one from Hydration Technologies Inc. (Albany, OR, USA). The Aquaporin Inside^{TM} (AIM) membrane is a modified TFC membrane with an active layer (AL) containing aquaporin proteins (AqpZ) reconstituted in spherical vesicles and encapsulated by a PA thin film supported by polyethersulfone (PES).[25,26] The Hydration Technologies Inc. (HTI) is a TFC membrane prepared using polyamide embedded (PA) in a polysulfone support.

FO experimental set-up

FO experiments were performed using a rectangular membrane module with a 140 cm^2 membrane area separating two identical compartments measuring 175 mm (length) by 80 mm (width) and 1.3 mm (height). The membrane AL faced the FS side (AL-FS mode), and a mesh spacer was installed on the support side. Counter-current circulation of the feed and draw solutions was applied using variable micro gear pumps (WT3000-1JB/M, Longer Pump, China) connected with Tygon®-tubing (R-3603) and operated at a flow rate of 260 $mL \cdot min^{-1}$ to generate a cross-flow velocity (u_{cr}) of 4.17 $cm \cdot s^{-1}$ according to the standard protocol of Aquaporin A/S, Denmark, and found in the study of Yoon et al. [27] using a u_{cr} of 4 $cm \cdot s^{-1}$. Furthermore, a 2 M NaCl model draw solution was used to generate an osmotic pressure difference across the FO-membrane or membranes, which were also used in the study of Widjojo et al. [28].

At the beginning of each experiment, 2 L of each feed and draw solution was placed in 5 L reservoirs. Changes in the electrical conductivity (EC, $mS \cdot cm^{-1}$) and mass (weight, kg) of the draw solution were recorded every 5 min using a conductivity probe (CDC 40101, Hach, Sweden) connected to a handheld metre (HQ30d, Hach, Sweden) and an electronic balance (FKB36K0.1, Kern & Sohn GmbH, Germany), respectively. All experiments were carried out at controlled room-temperature 20°C±2°C, and the duration of each experiment was at least 4 h. Furthermore, the dilution factor (DF) of the draw solution was set to 1.4 to easily compare the FO-experiments and maintain enough volume for laboratory analyses, especially BOD_7 analysis. A schematic diagram of the laboratory FO-set-up is shown in Figure 2.

Experiments

All conducted FO-experiments are summarized in Table 1 with their corresponding feed- and draw-solutes and the applied membrane(s).

Analytical methods

Depending on the experiment, grab samples were obtained at the sampling points shown as black dots in Figure 1, i.e. Raw, MSF, MFP. The suspended solids (SS), biochemical oxygen demand (BOD_7), chemical oxygen demand (COD), total organic carbon (TOC), total and soluble nitrogen (TNt, TNs), and total and soluble phosphorus (TPt, TPs) contents were measured using international standard methods. The total amount of volatile fatty acids (VFA) and alkalinity (Alk.) were measured using the 5 pH-point titration method [29] and incorporated with pH and electric conductivity (EC) measurements; for additional details see.[30] Samples were also collected from the draw solution (2 M NaCl) before and after each FO experiment. Regarding the Swedish discharge demands for small- to medium-sized WWTPs, BOD_7, TPt and TPs were measured in the feed and draw solutions at the beginning and end of each experiment.

Fouling autopsy

Fouled membrane samples were retrieved from the FO membrane module at the end of operation and stored in the fridge at 4°C before analysis. A scanning electron microscope (SEM) (Quanta FEG 200 ESEM^{TM}, FEI, USA) was used to capture membrane surface images. Before SEM, the samples were dried at room temperature and coated with gold. The composition of the deposited layer on the membrane surface was analysed using energy dispersive X-ray spectrometry (EDS) (Oxford Instruments AZtec EDS with X-Max detector, Oxford Instruments, UK). Samples were studied using an accelerating voltage of 10 kV and a working distance of 10 mm. Qualitative and quantitative analyses were based on internal standards using Aztec software.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used to identify the foulant functional groups (Spectrophotometer, PerkinElmer, USA equipped with a diamond crystal). ATR-FTIR spectra were recorded within the range of 4000-500 cm^{-1} with a resolution of 4 cm^{-1} using 4 scans at a temperature of 20°C±0.5°C. These spectra were subtracted against a background air spectrum, corrected for offset, normalized, and presented as transmittance (%).

Data analysis

The water flux (J_w, $L \cdot m^{-2} \cdot h^{-1}$) was determined using an electronic balance and monitoring the rate at which the weight of the draw solution increased. The achieved water flux was normalized (J/J_0) for comparison between experiments by dividing the water flux (J_W) with the initial water flux (J_0). Furthermore, no addition of, e.g., salt, during the experiment was performed to compensate for the dilution of the draw solution.

Solute rejection ($R_{(1)}$, %) was calculated as follows:

$$R_{(1)} = 1 - \frac{c_{Permeate}}{c_{Feed(Avg.)}} \cdot 100\% \quad \text{(Eq. 1)}$$

where $R_{(1)}$ (%) is the solute rejection, $c_{Permeate}$ ($mg \cdot L^{-1}$) is the concentration in the permeate, and $c_{Feed(Avg.)}$ ($mg \cdot L^{-1}$) is the average concentration in the feed solution during the experiment, see Liu et al. [31].

The average concentration in the FS was calculated as follows:

$$c_{Feed(Avg.)} = \frac{c_{Feed(t=0)} + c_{Feed(t=End)}}{2} \quad \text{(Eq. 2)}$$

where $c_{Feed(t=0)}$ ($mg \cdot L^{-1}$) is the initial concentration and $c_{Feed(t=End)}$ ($mg \cdot L^{-1}$) is the final concentration in the FS, respectively.

Osmotic pressure is the main driving force of FO; thus, the FO process naturally attempts to achieve osmotic equilibrium through the transport of water molecules from the FS to the draw solution. This water transport can be directly measured as the change in the volume (weight) of the draw solution during the FO experiment. The additional volume (weight) in the draw solution ($V_{Permeate}$, L) is described as the permeate. Because the permeate directly enters the draw solution, the permeate concentration ($c_{Permeate(1)}$, $mg \cdot L^{-1}$) cannot be directly measured. Therefore, mass balance was used and it was assumed that no measurable concentrations of the considered wastewater compounds were present in the draw solution ($c_{Permeate(t = 0)}$ = 0 $mg \cdot L^{-1}$) at the beginning of the experiment (t = 0):

$$c_{Permeate(1)} = \frac{V_{Draw(t = End)} \cdot c_{Draw(t = End)}}{V_{Permeate}} \text{ (Eq. 3)}$$

where $c_{Draw(t = End)}$ ($mg \cdot L^{-1}$) is the final concentration in the draw solution and $V_{Draw(t = End)}$ (L) is the final draw volume at the end of the experiment. $V_{Permeate}$ (L) is the transported volume across the FO membrane during the experiment, which is the difference between the final ($V_{Draw(t = End)}$, L) and initial ($V_{Draw(t = 0)}$, L) volumes of the draw solution.

By combining Eq. 2 and Eq. 3, the rejection $R_{(1)}$ can be expressed as follows:

$$R_{(1)} = 1 - \frac{\frac{V_{Draw(t = End)} \cdot c_{Draw(t = End)}}{V_{Permeate}}}{\frac{c_{Feed(t = 0)} + c_{Feed(t = End)}}{2}} \cdot 100\% \text{ (Eq. 4)}$$

Eq. 4 represents a standard method for calculating $R_{(1)}$, according to, e.g., Liu et al. [31]. However, the calculated solute rejection $R_{(1)}$ in Eq. 4 assumes that the initial concentration of the measured wastewater compounds, e.g., BOD_7, in the draw solution is 0 $mg \cdot L^{-1}$. Thus, when the initial concentrations are not zero, the concentration in the permeate ($c_{Permeate(2)}$, $mg \cdot L^{-1}$) can be calculated as follows:

$$c_{Permeate(2)} = \frac{V_{Draw(t=End)} \cdot c_{Draw(t=End)} - V_{Draw(t=0)} \cdot c_{Draw(t=0)}}{V_{Permeate}}$$ (Eq. 5)

where $V_{Draw(t=0)}$ (L) is the initial draw solution volume and $c_{Draw(t=0)}$ (mg·L^{-1}) is the initial concentration in the draw solution (see Xie et al. [32]).

Solute rejection, R_2 (%), including the initial amount of the measured compound in the draw solution, can be calculated as follows:

$$R_{(2)} = 1 - \frac{\frac{V_{Draw(t=End)} \cdot c_{Draw(t=End)} - V_{Draw(t=0)} \cdot c_{Draw(t=0)}}{V_{Permeate}}}{\frac{c_{Feed(t=0)} + c_{Feed(t=End)}}{2}} \cdot 100\%$$ (Eq. 6).

The results for R_1 and R_2 are shown in Table 3.

Results and Discussion

The tested configurations (see Figure 1) were intended to treat municipal wastewater at small- and medium-sized WWTPs (10 000 PE) to fulfil the Swedish discharge demands (BOD_7 15 mg·L^{-1}, TPt 0.5 mg·L^{-1}). TNt and TNs rejection were not considered because they were required for WWTPs larger than 10 000 PE, which require the removal of 85% of the TN entering the WWTP.[12] Furthermore, the final treatment of the generated concentrates, i.e., the sludge from the MS and the retentates from the MF and FO, were not part of the current investigation because fulfilment of the Swedish discharge demands was considered the primary step towards non-biological wastewater treatment of the main stream. However, studies have shown that, for example, more biogas (>30%) could be produced with mechanical or physicochemical pre-treatment in combination with membrane technology utilizing more of the total and soluble carbon in comparison to conventional wastewater treatment.[24,33,34] Wang et al. [15], anticipated that the treatment scenario should be energy-positive and economically beneficial when concentrating COD with FO at

average levels of 2335 $mg \cdot L^{-1}$ in combination with anaerobic digestion and downstream treatment.

The characteristics of the different feed types Raw, MSF and MFP (see Figure 1) that were subjected to the AIM and HTI membranes are shown in Table 2. The measured concentrations correspond with the results of Hey et al. [24], who used mechanical pre-treatment methods, i.e., MS before DMF.

Water fluxes

The normalized water fluxes (J/J_0) of different feed types (Raw, MSF, MFP) are shown in Figure 3a (AIM membranes) and Figure 3b (HTI membranes), respectively. The measured water fluxes ($L \cdot m^{-2} \cdot h^{-1}$) and EC ($mS \cdot cm^{-1}$) can be found in the Supplementary material (Figures A.1).

The AIM membranes exhibited similar flux patterns for the raw wastewater (Exp. 1), MSF (Exp. 2) and MFP (Exp. 3). The water fluxes remained stable and increased when mechanical pre-treatment steps were included in comparison to using raw wastewater (Raw). However, no significant difference in the observed water fluxes between MSF and MFP were observed, indicating that the water flux remains stable with increasing pre-treatment steps, as shown in Figure 3a.

The HTI membrane had higher initial water fluxes compared to the AIM membrane, but the water flux declined steadily for all of the tested feed types. The water flux from the MSF was lower than the water flux from the MFP (see Figure 3b), indicating that the water flux increases as the number of mechanical pre-treatments increases.

In Experiment 1, when raw wastewater was used as feed in FO with the AIM membrane, the water flux decreased by 25% during the first 3 h from an initial normalized water flux 1 (J/J_0) to a final flux of 0.75 (J/J_0). Thereafter, the water flux

remained relatively stable until the end of the experiment (Figure 3a). The normalized water flux through the HTI membrane decreased linearly by 43% from 1 (J/J_0) to 0.57 (J/J_0) suggesting that HTI membranes are more sensitive to fouling by suspended solids than AIM (Figure 3b).

In Experiment 2, MS with an aperture size of 100 µm was used before FO (SS 250 $mg \cdot L^{-1}$, see Table 2), and the water flux was higher than for the raw wastewater (Raw) flux pattern for the AIM membrane. The normalized water flux of the AIM membrane was higher (J/J_0: 0.93) than the water flux through the HTI (J/J_0: 0.75), as shown in Figures 3a and 3b.

The particle free (SS=0 $mg \cdot L^{-1}$) MFP was assumed to positively affect the FO performances of both the AIM and HTI membranes. The normalized water flux decreased from 1 (J/J_0) to 0.87 (J/J_0) for the AIM membrane, see (Figures 3a) and for the HTI membrane 0.83 (J/J_0) for the HTI membrane, see Figure 3b.

The decreased water flux during FO results from a decrease in the osmotic driving force (DF ~1.4) and concentration polarization (CP) phenomena.[26] CP results in the formation of a solute concentration gradient near the membrane surface and a local increase (or decrease) in osmotic pressure. Thus, organic molecules accumulate, which promotes membrane fouling [35] and decreased water flux.

The corresponding water fluxes (J_W, $L \cdot m^{-2} \cdot h^{-1}$), see Figure A.1 in the supplementary material, of the AIM and HTI membranes agree with those observed by Wang et al. [36], who tested raw wastewater (after screening with 900 µm) in the AL-FS mode (TFC HTI) by using NaCl as the draw solution. Wang et al. [15] achieved an average water flux rate of 6 $L \cdot m^{-2} \cdot h^{-1}$ with diluted wastewater and used 0.5 M NaCl as the model draw solution when using a cellulose triacetate membrane (CTA) from HTI. Similar values were also obtained by Holloway et al. [37], who reported water fluxes of

10.1 $L \cdot m^{-2} \cdot h^{-1}$ for concentrated anaerobic digests using CTA membranes from HTI. Zhang et al. [38] tested synthetic urine and achieved water fluxes within the range of 4 to 18 $L \cdot m^{-2} \cdot h^{-1}$, depending on the employed draw solution concentrations (ranging from 0.5 to 2 M NaCl) in the absence of particles, e.g., suspended solids (SS).

Solute rejections

To evaluate the impacts of MS and MF on FO performance and subsequent fouling propensity, the physical and chemical properties of mechanically pre-treated wastewater were analysed, see Table 2.

For small- and medium-sized WWTPs in Sweden, BOD_7 reductions of 70-90% and TP reductions of 80% are required.[12] To consider FO as a potential technology for municipal wastewater treatment without the biological treatment step, the required BOD_5 and TP reductions must be met. Table 3 shows the calculated solute rejection (%) from using different tested feed types (Exp. 1-3) for the AIM and HTI membranes. The final concentration ($c_{Permeate(2)}$) can be found in the Supplementary material (Table A.1).

Generally, both membranes displayed rejection levels >96%, with the AIM membrane displaying slightly higher rejection levels than the HTI membrane. Both of the FO-membrane treatments revealed a high BOD_7 rejection (above 96%), which was calculated using the extended solute-rejection equation (Eq. 6) in all experiments. The lower BOD_7 rejection of the MFP (AIM: 98%; HTI: 96%) can be attributed to the initial BOD_7 concentration in the permeate (19 $mg \cdot L^{-1}$) compared to the raw (250 $mg \cdot L^{-1}$) and MSF (150 $mg \cdot L^{-1}$) (see Table 2). Despite the availability of FO studies that considered complex wastewater, no studies have reported BOD_7 rejection, which is a parameter for WWTPs with discharge requirements. Nevertheless, because the BOD is a fraction of the COD and TOC,[39] a COD rejection of more than 99% (raw wastewater) and a

TOC rejection of more than 94% (synthetic wastewater) were reported by Wang et al. [15] and Xue et al. [22], respectively. Furthermore, Madsen et al. [40] showed high rejections of trace organic compounds when using AIM membranes. These results imply high BOD rejections.

Furthermore, TPt and TPs rejection was always greater than 97%. High phosphorus rejection (>95%) was found in other studies using CTA FO-membranes, in which higher rejections were expected with TFC membranes, regardless of the type of wastewater feed considered.[15,37,41,42] The mean pore size of cellulose-based FO membranes is 0.74 nm,[32] consequently, hydrated phosphorus, with a radius of 0.49 nm, can be rejected. High phosphorus rejection is a result of not only size exclusion but also charge repulsion because the membrane and phosphates ions are negatively charged when the pH is greater than 7.[21,43,44] Additionally, Xue et al. [22] demonstrated that higher phosphate rejections can be achieved by increasing the pH to >7 due to the transformation of $H_2PO_4^-$ to HPO_4^{2-} at pKa=7.2. This transformation could explain the high TPt and TPs rejection observed in this study because the initial pH of the feed and draw solutions was always >7.5.

Evaluation of membrane fouling

Scanning electron microscope (SEM) observations of fouled AIM and HTI membranes demonstrated that a fouling layer covers the surface of all membranes (Figures A.2, A.4, A.6, A.10, A.12, and A.14 in the Supplementary material). Consequently, a reduced mass transfer across the membrane is expected due to increased membrane resistance and the cake enhanced concentration polarization effect.[45] However, as shown by the AIM and HTI permeate fluxes (see Figures 3a and 3b), severe fouling does not occur in the AL-FS configuration, which agrees with the results reported by Zhang et al. [46]. Furthermore, the presence of bacteria was noticed on both AIM and

HTI membranes after adsorptive fouling with Raw and MSF feed (Figures A.2, A.4, A.10, and A.12 in the Supplementary material). Additionally, the EDS analysis revealed the presence of N and P on the fouled AIM and HTI membranes, which suggested biofouling and the presence of extracellular polymeric substances (EPS). This is in agreement with the results of Zhang et al. [46] and Xue et al. [47]. In addition, more bacteria were present on the AIM membranes than on the HTI membranes after drainage due to bacterial growth on/in the MS. Thus, rougher and more negatively charged AIM membranes appear more prone to biofouling. Yet, the decrease of water flux for AIM membranes (Figure 3a) over time is less pronounced than that for the HTI membrane (Figure 3b). When combined with the slightly higher rejection levels for the AIM membranes than the HTI membrane (see Table 2), this result points to the possible beneficial effects of moderate levels of biofouling. Based on the SEM study, no bacteria were found on the membranes when considering the MFP with no evidence of biofilm. This suggests that microorganisms were removed by the MF pre-treatment, which agrees with the results of Kolega et al. [49] who reported absence of total coliforms and faecal streptococcus in the DMF-permeate of primary treated sewage. The composition of the resulting deposits indicated that Ca, Fe and Al and Si (Fig. A.3, A.5, A.7, A.11, A.13 and A.15 in Supplementary material) were the main foulants, in addition to the membrane fabric elements C and O, which agrees with the results reported by Zhang et al. [46]. In addition, HTI membrane fouling resulted from raw wastewater that contained more calcium than iron, and the opposite effect was observed for the AIM (Figures A.3 and A.11 in the Supplementary material). The enhanced iron deposition on the surface of the AIM membrane probably resulted from the higher negative charge of the membrane. This is probably caused by the presence of negatively charged AqpZ incorporated in the PA thin film.[48] The likelihood of iron,

which has a positive three charge, bonding with a negatively charged carboxylic group of the PA thin film AqpZ TFC layer is higher than that of the more neutral HTI membrane containing only TFC PA layer. However, more calcium is bound to the HTI membrane, which could explain the HTI fouling and the lower water flux obtained for the HTI membranes. The presence of silica on the surfaces of the AIM and the HTI membranes after adsorptive fouling with MFP agrees with the results presented by Li et al. [50], Zhao et al. [26], and Mi and Elimelech [51]. This presence could accelerate fouling by organic matter.

To further understand the fouling of FO membranes when treating municipal wastewater, ATR-FTIR was used to investigate clean and fouled AIM and HTI membranes. Figures 4 and 5 show the main functional groups for both the selective and support layer: polyethersulfone (PES) for the AIM membrane or polysulfone (PS) for the HTI membrane. The characteristic spectra of the polyamide thin film of the AIM membrane (Figure 4) were observed at 1739 cm^{-1} (C=O stretching, carboxylic acid groups), 1658 cm^{-1} (C=O stretching, amide I), and 1578 cm^{-1} (C-N stretching, amide II). For the polyethersulfone support, peaks were found at 1486 cm^{-1}, 1298 cm^{-1} (SO_2, asymmetric stretch), 1242 cm^{-1} (aryl-O-aryl, C-O stretch), 1152 cm^{-1} (SO_2, symmetric stretch), and 1106 cm^{-1} (skeletal aliphatic C-C/aromatic hydrogen bending/rocking).[52]

However, as shown in Figure 4, the intensities of the characteristic peaks for the polyamide layer generally decreased due to adsorptive fouling when considering the Raw and MSF effluents. The ATR-FTIR spectra for fouled membranes (Raw and MSF) exhibited new bands at 3295 cm^{-1}, 2921 cm^{-1} and 2851 cm^{-1}, which are unique for polysaccharides,[53] and at 1641 cm^{-1} and 1576 cm^{-1}, which are characteristic of the secondary structure of proteins (amide I and II).[52] This result indicates that proteins

and polysaccharides are the main organic foulants, which agrees with the results reported by Wang et al. [55] and Zhang et al. [46]. After MF treatment, the polysaccharide and protein signals were reduced compared with the Raw and MSF filtrates, which could explain the higher observed water fluxes for MFP.

For the clean HTI membrane, the bands for the selective polyamide and polysulfone support layers were found at 1716 cm^{-1} (C=O, carboxylic acid groups stretching), 1488 cm^{-1} (CH_3-C-CH_3, stretching), and 1417 cm^{-1} (C=C aromatic ring stretching) and at 1170 cm^{-1}, 1150 cm^{-1} and 1105 cm^{-1} (skeleton aliphatic C-C/aromatic hydrogen bending, rocking).[52] The spectra of the fouled HTI membranes subjected to MSF feed are characteristic of proteins at 1639 cm^{-1} and 1541 cm^{-1} and polysaccharides at 1047 cm^{-1}.[53,54] Although polysaccharides and proteins were removed during the MF step, the membrane signal of the membrane exposed to MFP was lower than the membrane signal of the clean membrane (Figure 5). Thus, the deposit covering the HTI membrane was likely caught inside, which resulted in lower water flux (Figure 3c). However, the reasons behind this finding remain unclear.

Conclusions

This study demonstrates combining FO and mechanical pre-treatment for raw municipal wastewater treatment and microsieving, which could be used to treat municipal wastewater at small- and medium-sized WWTPs, to fulfil Swedish discharge requirements. AIM and HTI membranes both achieved a stable normalized water flux, with rejection rates of more than 96% for BOD_7, TPt and TPs, regardless of the mechanical pre-treatment used. Using raw wastewater to feed FO resulted in the highest water flux loss, with a loss of 25% for AIM and 43% for HTI, respectively, relative to the mechanically pre-treated effluents. No significant difference in water flux was found when comparing MS and MF for pre-treatment before FO; however, the HTI

membrane generally revealed a higher decrease in the initial water flux over time compared to the AIM membrane.

In all tests, the higher initial water flux of the HTI membrane was cancelled out by a higher water flux loss over time. From these observations, and considering the fact that the highest water flux loss occurred with raw wastewater, the results indicate that the HTI membrane is more prone to fouling and concentration polarization phenomena (and needs several pre-treatment steps to maintain a high normalized water flux).

The prevailing foulant during FO was organic, consisting mainly of proteins, polysaccharides, and microorganisms. The deposited material also contained inorganic elements, such as Ca, Fe, Al and Si. Pre-treatment with MF reduced fouling; hence, less membrane area and cleaning would be required. However, HTI membrane fouling cannot be fully avoided, even when including a MF step, because the deposits on the membrane hinder water transport across the membrane. Therefore, more work is still required to address membrane fouling issues to optimize membrane performance.

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Appendix A. Supplementary materials

Supplementary data, tables and figures associated with this article can be found in the online version.

References

[1] Lazarova V, Choo K-H, Cornel P. Water-energy interactions in water reuse. London, UK: IWA Publishing; 2012.

[2] Rodriguez-Caballero A, Aymerich I, Poch M, et al. Evaluation of process conditions triggering emissions of green-house gases from a biological wastewater treatment system. Sci Total Environ. 2014;493:384-391.

[3] Ravazzini AM, van Nieuwenhuijzen AF, van der Graaf JHMJ. Direct ultrafiltration of municipal wastewater: comparison between filtration of raw sewage and primary clarifier effluent. Desalination. 2005;178:51-62.

[4] Van Nieuwenhuijzen AF, Evenblij E, van der Graaf JHMJ. Direct wastewater membrane filtration for advanced particle removal from raw wastewater. In: Hahn HH, Hoffmann E, Ødegaard H, editors. Chemical water and wastewater treatment VI. Berlin: Springer Verlag; 2000.

[5] Sayed S, Tarek S, Dijkstra I, et al. Optimum operation conditions of direct capillary nanofiltration for wastewater treatment. Desalination. 2007;214:215-226.

[6] Van Nieuwenhuijzen AF. Scenario studies into advanced particle removal in the physical-chemical pre-treatment of wastewater. Delft, Netherlands: Delft University Press; 2002. p. 129.

[7] Lateef SK, Soh BZ, Kimura K. Direct membrane filtration of municipal wastewater with chemically enhanced backwash for recovery of organic matter. Bioresour Technol. 2013;150:149-155.

[8] Ahn KH, Song JH, Yeom IT, et al. Performance comparison of direct membrane separation and membrane bioreactor for domestic wastewater treatment and water reuse. Water Science and Technology: Water Supply. 2001;1:315-323.

[9] Ahn K, Song J, Cha H. Application of tubular ceramic membranes for reuse of wastewater from buildings. Water Sci. Technol. 1998;38:373-382.

[10] Ahn K, Song K. Application of microfiltration with a novel fouling control method for reuse of wastewater from a large-scale resort complex. Desalination. 2000;129:207-216.

[11] Ramona G, Green M, Semiat R, et al. Low strengthg reywater characterization and treatmentby direct membrane filtration. Desalination. 2004;170:241-250.

[12] Council of the European Union. 1991. Council Directive 91/271/EEG concerning urban waste water treatment. Official Journal of the European Communities.

[13] Council of the European Union. 1998. Commission Directive 98/15/EC, amending council directive 91/271/EEC with respect to certain requirements established in Annex I thereof. Official Journal of the European Communities.

[14] Council of the European Union. 2015. Commission implementing decision 2015/495/EU establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to directive 2008/105/EC of the European Parliament and of the Council. Official Journal of the European Union.

[15] Wang Z, Zheng J, Tang J, et al. A pilot-scale forward osmosis membrane system for concentrating low-strength municipal wastewater: performance and implications. Sci Rep. 2016;6:21653.

[16] Xie M, Kyong Shonb H, Greya SR et al. Membrane-based processes for wastewater nutrient recovery: technology, challenges, and future direction. Water Res. 2016;89:210-221.

[17] Coday BD, Xu P, Beaudry EG, et al. The sweet spot of forward osmosis: treatment of produced water, drilling wastewater, and other complex and difficult liquid streams. Desalination. 2014;333:23–35.

[18] Lutchmiah K, Verliefde AR, Roest K, et al. Forward osmosis for application in wastewater treatment: a review. Water Res. 2014;58:179-197.

[19] Alturki AA, McDonald JA, Khan SJ, et al. Removal of trace organic contaminants by the forward osmosis process. Sep Purif Technol. 2013;103:258–266.

[20] Cui Y, Ge Q, Liu X, et al. Novel forward osmosis process to effectively remove heavy metal ions. J Membr Sci. 2014;467:188-194.

[21] Valladares Linares R, Yangali-Quintanilla V, Li Z, et al. Rejection of micropollutants by clean and fouled forward osmosis membrane. Water Res. 2011;45:6737-6744.

[22] Xue W, Tobino T, Nakajima F, et al. Seawater-driven forward osmosis for enriching nitrogen and phosphorous in treated municipal wastewater: effect of membrane properties and feed solution chemistry. Water Res. 2015;69:120-130.

[23] Xie M, Nghiem LD, Price WE et al. A forward osmosis–membrane distillation hybrid process for direct sewer mining: system performance and limitations. Environ Sci Technol. 2013;47:13486–13493.

[24] Hey T, Vänäänen J, Heinen N et al. Potential of combining mechanical and physicochemical municipal wastewater pre-treatment with direct membrane filtration. Environ Technol. 2016. In press.

[25] Yip NY, Tiraferri A, Phillip WA, et al. High performance thin-film composite forward osmosis membrane. Environ Sci Technol. 2010;44:3812-3818.

[26] Zhao S, Zou L, Tang CY, et al. Recent developments in forward osmosis: opportunities and challenges. J Membr Sci. 2012;396:1-21.

[27] Yoon H, Baek Y, Yu J et al. Biofouling occurrence process and its control in the forward osmosis. Desalination 2013;325:30-36.

[28] Widjojo N, Chung TS, Weber M et al. The role of sulphonated polymer and macrovoid-free structure in the support layer for thin-film composite (TFC) forward osmosis (FO) membranes. J Membrane Sci. 2011;383:214-223.

[29] Moosbrugger RE, Wentzel MC, Ekama GA, et al. A 5 pH point titration method for determining the carbonate and SCFA weak acid/bases in anaerobic systems. Water Sci Technol. 1993;28:237-245.

[30] Hey T, Jönsson K, la Cour Jansen J. Full-scale in-line hydrolysis and simulation for potential energy and resource savings in activated sludge – a case study. Environ Technol. 2012;33:1819-1825.

[31] Liu P, Zhang H, Feng Y, et al. Influence of spacer on rejection of trace antibiotics in wastewater during forward osmosis process. Desalination. 2015;371:134-143.

[32] Xie M, Nghiem LD, Price WE, et al. Comparison of the removal of hydrophobic trace organic contaminants by forward osmosis and reverse osmosis. Water Res. 2012;46:2683-2692.

[33] Remy C, Boulestreau M, Lesjean B. Proof of concept for a new energy-positive wastewater treatment scheme. Water Sci. Technol. 2014;70:1709-1716.

[34] Juby GJG, Sethi S, Deshmukh SS et al. Reducing costs by producing methane instead of WAS: the IMANS™ approach to treatment and reclamation. Proceedings of the Water Environment Federation, WEFTEC 2001;11:140-150.

[35] Sheikholeslami R. Fouling of membrane and thermal units: a unified approach to its principles, assessment, control and mitigation. L'Aquila, Italy: Desalination Publications; 2007.

[36] Wang Z, Tang J, Zhu C, et al. Chemical cleaning protocols for thin film composite (TFC) polyamide forward osmosis membranes used for municipal wastewater treatment. J Membr Sci. 2015;475:184-192.

[37] Holloway RW, Childress AE, Dennett KE, et al. Forward osmosis for concentration of anaerobic digester centrate. Water Res. 2007;41:4005-4014.

[38] Zhang J, She Q, Chang VW, et al. Mining nutrients (N, K, P) from urban source-separated urine by forward osmosis dewatering. Environ Sci Technol. 2014;48:3386-3394.

[39] Henze M, Harremoës P, la Cour Jansen J, et al. Wastewater treatment: biological and chemical processes. Berlin: Springer Verlag; 2002.

[40] Madsen HT, Bajraktari N, Hélix-Nielsen N et al. Use of biomimetic forward osmosis membrane for trace organics removal. J Membrane Sci. 2015;476:469-474.

[41] Xie M, Price WE, Nghiema LD et al. Effects of feed and draw solution temperature and transmembrane temperature difference on the rejection of trace organic contaminants by forward osmosis. J Membrane Sci. 2013;438:57–64.

[42] Xie M, Price WE, Nghiema LD et al. Relating rejection of trace organic contaminants to membrane properties in forward osmosis: Measurements, modelling and implications. Water Res. 2014;49:265–274.

[43] Van Voorthuizen EM, Zwijnenburg A, Wessling M. Nutrient removal by NF and RO membranes in a decentralized sanitation system. Water Res. 2005;39:3657-3667.

[44] Nguyen NC, Chen S.-S, Yang H.-Y, et al. Application of forward osmosis on dewatering of high nutrient sludge. Bioresour Technol. 2013;132:224-229.

[45] Hoek EM, Elimelech M. Cake-enhanced concentration polarization: A new fouling mechanism for salt-rejecting membranes. Environ Sci Technol. 2003;37:5581-5588.

[46] Zhang J, Loong WLC, Chou S, et al. Membrane biofouling and scaling in forward osmosis membrane bioreactor. J Membr Sci. 2012;403-404:8-14.

[47] Xue W, Yamamoto K, Tobino T. Membrane fouling and long-term performance of seawater-driven forward osmosis for enrichment of nutrients in treated municipal wastewater. Journal of Membrane Science. 2016;499:555-562.

[48] Ding W, Cai J, Yu Z et al. Fabrication of an aquaporin-based forward osmosis membrane through covalent bonding of a lipid bilayer to a microporous support. Journal of Materials Chemistry A. 2015;3:20118-20126.

[49] Kolega M, Grohmann GS, Chiew RF, et al. Disinfection and clarification of treated sewage by advanced microfiltration. Water Sci Technol. 1991;23:1609-1618.

[50] Li Z.-Y, Yangali-Quintanilla V, Valladares-Linares R, et al. Flux patterns and membrane fouling propensity during desalination of seawater by forward osmosis. Water Res. 2012;46:195-204.

[51] Mi B, Elimelech M. Silica scaling and scaling reversibility in forward osmosis. Desalination. 2013;312:75-81.

[52] McCutcheon JR, Hoek EMV, Bui N, et al. Nanostructured membranes for engineered osmosis applications. Google Patents, 2013. US 20130105395 A1. http://www.google.com/patents/US20130105395.

[53] Xu P, Drewes JE, Kim T, et al. Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications. J Membrane Sci. 2006;279:165-175.

[54] Maruyama T, Katoh S, Nakajima M, et al. FT-IR analysis of BSA fouled on ultrafiltration and microfiltration membranes. J Membrane Sci. 2001;192:201-207.

[55] Wang X, Yuan B, Chen Y, et al. Integration of micro-filtration into osmotic membrane bioreactors to prevent salinity build-up. Bioresour Technol. 2014;167:116-123.

Table 1. Conducted FO-experiments with different feed types and tested membranes.

Experiment	Feed solution	Draw solution	Membrane type
Exp. 1	Raw municipal wastewater (Raw)	2 M NaCl	AIM, HTI
Exp. 2	Microsieve filtrate (MSF)	2 M NaCl	AIM, HTI
Exp. 3	Microfiltration permeate (MFP)	2 M NaCl	AIM, HTI

Table 2. Characteristics of the feed types and the concentrations ($mg \cdot L^{-1}$) of the raw wastewater (Raw), microsieve filtrate (MSF) and microfiltration permeate (MFP). EC is shown in $mS \cdot cm^{-1}$.

	SS	BOD_7	CODt	TOCt	TPt	TPs	TNt	TNs	Alk.	VFA	EC
Raw	440	250	560	110	9.1	2.4	61	52	290	23	0.9
MSF	250	150	410	89	9.0	1.9	35	28	232	13	0.8
MFP	0	19	73	55	1.9	1.7	34	26	230	7	0.8

Table 3. Solute rejections of biochemical oxygen demand (BOD_7) and the total and soluble phosphorus (TPt, TPs) of the tested feed types (Raw, MSF and MFP) using FO AIM and HTI membrane. The R_2 values for solute rejection, including the initial concentration in the draw solution compared to the solute rejection value R_1, are shown in parentheses.

Feed	**Membrane**	**BOD_7**	**TPt**	**TPs**
Raw	AIM	100% (97%)	99% (97%)	98% (97%)
	HTI	99% (98%)	98% (98%)	97% (97%)
MSF	AIM	100% (97%)	100% (100%)	98% (96%)
	HTI	99% (97%)	99% (99%)	98% (97%)
MFP	AIM	98% (77%)	99% (98%)	98% (98%)
	HTI	96% (85%)	98% (98%)	98% (98%)